Increase in Atmospheric Column of CHClF$_2$ (HCFC-22) over Southern California from 1985 to 1990.

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-<u>Abstract</u>. Column densities of CHClF$_2$ (HCFC-22) have been measured over Table Mountain Observatory, Wrightwood, CA (34.4°N) using the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier-transform infrared (FTIR) spectrometer. Between October, 1985 and July, 1990, the column increase rate was $(6.5 \pm 0.5)\%$ yr^{-1}. From CHClF$_2$ to N$_2$O ratio results, good agreement was found between CHClF$_2$ columns presented here and previously published in-situ measurements. Combining these measurements, a CHClF$_2$ accumulation rate of $(6.5 \pm 0.3)\%$ yr^{-1} between October, 1985 and December, 1992 was determined. Column measurements of CHClF$_2$ over McMurdo Sound, Antarctica (78°S) in September and October, 1986 by the MarkIV FTIR spectrometer were used to determine a south-north interhemispheric ratio of (0.85 ± 0.08). The feasibility of using CHClF$_2$ column measurements to determine a globally averaged chemical lifetime for CHClF$_2$, or equivalently, a global estimate of the OH field was also investigated, An adequate estimate of the global OH field cannot be made without reducing the uncertainty in historical CHClF$_2$ emission estimates.

Introduction

Concern over the ozone layer has required the increasing use of hydrogenated halocarbons, such as CHClF$_2$ (HCFC-22), as an alternative to fully halogenated species, such as CCl$_2$F$_2$ (CFC-12) and CCl$_3$F (CFC-11). CHClF$_2$ and other hydrogenated halocarbons can react with OH radicals, thus their tropospheric lifetimes have been calculated to be significantly shorter than those of CCl$_2$F$_2$ and CCl$_3$F (e.g., 16 years for CHClF$_2$ [Golombek and Prinn, 1989] vs. 111 years for CCl$_3$F and 74 years for CCl$_2$F$_2$ [W, M. O., 1989, pg. 547]). As its tropospheric lifetime is relatively short, the contribution of CHClF$_2$ to inorganic chlorine in the stratosphere has been estimated to be quite small (1%) [Weisenstein et al., 1992]. However, as Solomon et al. [1992] report, the long stratospheric lifetime of CHClF$_2$ may contribute to greater ozone depletion from its reaction products than that predicted by many gas-phase models in the lower stratosphere. Accurate prediction of changes in stratospheric ozone and global climate warrants continued monitoring of CHClF$_2$.

Previous measurements have shown $CHClF_2$ to be increasing rapidly in the troposphere. Among recent reports, Montzka et al. [1993], using in-situ techniques, determined an exponential rate of increase of $(7.3 \pm 0.3)\%$ yr^{-1}, and a linear rate of increase of (6.3 ± 0.3) pptv yr^{-1} in the global mean ground-level concentration of $CHClF_2$ between 1987 and December, 1992. Total column measurements reported by Zander et al. [1993] show an increase of $(7.0 \pm 0.35)\%$ yr^{-1} over the Jungfraujoch, Switzerland (46.5°N) from 1986 to 1992, and $(7.0* 0.23)\%$ yr^{-1} over Kitt Peak, AZ (31.9°N) from 1980 to 1992, In this study we report measurements taken by the ATMOS spectrometer over Table Mountain, CA , and calculate the column accumulation rate between October, 1985 and July, 1990.

Column measurements by the MkIV FTIR spectrometer over McMurdo Sound in 1986 can be evaluated for the interhemispheric ratio of $CHClF_2$, but these columns cannot be directl y compared to those in northern mid-latitudes because of the lower Antarctic tropopause. A possible basis for comparison is with estimates of the ground-level mixing ratio obtained by scaling an assumed a priori vertical mixing ratio profile by the same factor used to fit the column absorption, However, this technique is sensitive to the shape of the a priori profile.   ]nstead, a "self-contained" and simpler comparison may be made between ratios of the $CHClF_2$ column to that of N_2O, as N_2O is a long-lived tropospheric source gas that is destroyed in the stratosphere. We recognize that in some respects, a comparison of column $CHClF_2$ to CH4 may be more appropriate as CH4 is also destroyed by011, while N_2O is destroyed by photo] ysis. However, we note that N_2O is a longer-lived species than CH4, and has a lower rate of increase [W.M.O., 1989, pg. 547]. As some 90% of the atmospheric N_2O resides in the troposphere, the N_2O column can act as a surrogate for the tropospheric air burden, We combine our $CHClF_2/N_2O$ column ratios with ratios of in-situ $CHClF_2/N_2O$ measurements for comparison and estimation of the northern mid-latitude trend of $CHClF_2$ for 1985 to 1992.

We discuss the use of $CHClF_2$ measurement for inference of the global OH field, Current estimates of OH are based on scaling the OH field produced by chemical transport models to reproduce observed surface concentrations of meth yl chloroform, CH_3CCl_3 (e.g. Spivakovsky et al. [1992]; Prinn et al. [1992]). Differences in the inferred OH fields are discussed in terms of the probable error in historical emissions of $CHClF_2$.

Measurements and Data Analysis

The ATMOS instrument is designed for stratospheric measurements from the space shuttle [see Farmer et al., 1987], but is also suitable for ground-based retrievals of the column abundance of various gases [see Gunson and Irion, 1990], It has an unanodized resolution is 0.01 cm^{-1} and its fast

response time allows several interferograms to be taken within a narrow range of solar zenith angles, For this study, 4 to 100 successive, double-sided interferograms were transformed with the resulting spectra averaged, giving a signal-to-noise ratio in the averaged spectrum of at least 600:1. For results described here, the Mark IV FTIR spectrometer returned data with an unapodized spectral resolution of 0.007 cm^{-1} and a signal-to-noise ratio varying between 100:1 and 1200 to 1. Further details of this instrument, as well as experimental conditions at McMurdo Sound, may be found in Toon et al. [1989] and Toon et al. [1991].

Analysis software used for column retrievals from both instruments was described by Norton and Rinsland [1991]. Constituent and physical parameters were mapped into a 150 layer model atmosphere, each layer homogeneous and 1 km thick. For the ATMOS retrievals, the U. S. Standard Atmosphere [1976] was used for the temperature and pressure profile while daily rawinsonde data were used for McMurdo Sound retrievals. Synthetic spectra were calculated for small spectral intervals containing the target gas, and an assumed volume mixing ratio profile was scaled until the residual (observed - calculated) was minimized in a least squares manner, The peak of the $2\nu_6$ Q-branch at 829.05 cm^{-1} was used for $CHClF_2$ analyses. The N_2O lines used were the same as those used in Toon et al. [1989]. Line parameters were from the ATMOS main and supplemental linelists [see Drown et al., 1987]. Where two or more averaged spectra were available for a day, each spectrum was analyzed and the resulting columns averaged for the day's measurement. Figure 2 shows a typical ATMOS observed and calculated spectral region for $CHClF_2$, along with the spectral residual. Column N_2O for McMurdo Sound is from Toon et al. [19891]

instrumental Results and Discussion

$CHClF_2$ column results for Table Mountain, McMurdo Sound and, for comparison, Kitt Peak results of Zander et al. [1993] are shown in Figure 3. To directly compare Kitt Peak and TMF columns, retrieved columns were divided by the U.S. Standard Atmosphere [1976] pressure (in atmospheres) appropriate to the observation altitude. (We could not ratio $CHClF_2$ to N20 for this comparison as same-day N_2O measurements were not available for Kitt Peak,) Estimated errors are described in Table 1. A straight-line fit for Table Mountain results shows the column density (extrapolated to sea-level) increasing by $(1\ 1.5 \pm 0.09) \times 10^{13}$ molecules $cm^{-2}\ yr^{-1}$ (1a error) from October, 1985 to July, 1990. An exponential fit indicates an increase of $(6.7 \pm 0.5)\%\ yr^{-1}$, which compares well with the figure of $(7.0 \pm 0.23)\%\ yr^{-1}$ for Kitt Peak. No significant systematic difference can be seen between TMF and Kitt Peak, The same scaling factors used to fit the column absorption were used to estimate a ground-level volume mixing ratio, assuming the a priori profiles shown in Figure 1, Calculations for Table Mountain show an increase in the ground-level VMR

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from (70 ± 6) pptv in October, 1985 to $(99^* 8)$ pptv in August, 1990, the linear increase being $(s,9 \pm 0.4)$ pptv yr^{-1} (1 σ error). 'I'his agrees within error with the figure of (6.3 ± 0.3) pptv yr^{-1} reported by Montzka et al. [1993] for the period between 1987 and December, 1992.

Figure 4 shows the CHClF$_2$/N$_2$O column ratios from this work as well as ratios of in-situ measurements of CHClF$_2$ reported by Montzka et al. [1993] to month] y averaged measurements of N$_2$O taken as part of the ALE/GAGE program (prior to July, 1988) or extrapolations of fitted equations to those measurements (on or after July, 1988; see Prinn et al, [1990]). Measurements from Cape Meares, Oregon (45° N) were used to ratio the northern hemisphere in-situ measurements and measurements from Cape Grim, Tasmania (145"E) were used for the south. Agreement between the column and in-situ CHClF$_2$/N$_2$O ratios is good. From the McMurdo Sound observation and the fitted line for the northern hemisphere, wc calculate a south-north hemispheric ratio of (0.85 ± 0.08). This is in good agreement with Montzka et al. [1993], who reported an interhemispheric CHClF$_2$ difference of $(13^* 1)$ pptv and a 1992 mean southern hemisphere mixing ratio of (95.2 ± 2) pptv, giving a south-north ratio of (0.88 ± 0.04).

An exponential fit to the northern hemisphere data points shows a rate of increase in the CHClF$_2$ column of (6.5 ± 0.3) % yr^{-1} relative to N$_2$O. Taking the rate of increase of N$_2$O in the atmosphere to bc (0.28 ± 0.03)% yr^{-1} (see Prinn et al., 1990), the CHClF$_2$ column would then be increasing by (6.8 ± 0.3) % yr^{-1}, in agreement with the figure of (7.3 ± 0.3) % year^{-1} determined by Montzka et al. [1993] for the world-wide ground-level concentration increase between mid- 1987 to the end of 1992.

Model methodology and results

Model results were obtained using the 2-D chemical transport model developed by Tung [1982; 1986], Yang et al, [1991] and Olaguer et al. [1991]. The model domain extends from 90°S to 90°N with eighteen latitudinal bands and from O to 56 km with 24 vertical levels, The model has been validated for tracers which are sensitive to stratospheric and tropospheric chemical and transport parameters [Yang et al., 1991; Olaguer et al., 1992; Brown, 1993]. In particular, the model has been shown to produce modeled atmospheric concentrations of methyl chloroform consistent with observat ions. 'I'he modeled global] y averaged lifetime of methyl chloroform and CHClF$_2$ were 7.3 and 19 years respectively, The destruction of CHClF$_2$ by photodissociation and by chemical reaction with OH and O(^{1}D) were modeled with concentrations of CHClF$_2$ set to zero at the beginning of 1949, when the atmosphere is known to have no CHClF$_2$. The model was run forward in time to a model year equivalent to the end of 1992 using emission estimates of Jesson et al. [1979] prior to 1970, and Midgley and Fisher [1992] from 1970 to 1991. For 1992, an emission of 213 x 10^6 kg is

used (obtained by linear extrapolation of prior emission estimates). The uncertainty in emissions subsequent to 1970 were estimated to be +12.5% and -8.5% [Don Fisher, private communication, 1993].

Six experiments (E1-E6) were performed and modeled column densities of $CHClF_2$ were compared with observed column densities. The results are summarized in Figure 3. Experiment El, using emission estimates described above, overestimates column densities at both observation sites. These results reflect uncertainty in emission estimates and the model OH field. ExperimentsE2-E5 were designed to test the sensitivity of the model results to these uncertainties. Modifications to the 011 field and the $CHClF_2$ emission are summarized in Table 2. Note that the scaling of the OH field in experiments E3 and E4 yields a model calculated globally averaged $CHClF_2$ lifetime of 15.5 years, consistent with the estimate of Golombek and Prinn [1989], while that for E5 yields a $CHClF_2$ lifetime of 13.5 years, consistent with the estimate of Montzka et al. [1993], Average concentrations for all model experiments are summarized in 'Table 3. Experiments E2, E4 and E5 all yield model results consistent with observed column densities in the northern hemisphere.

Conclusions

$CHClF_2$ column retrievals from Table Mountain Facility indicate an increase rate (extrapolated to sea-level) of (1 1.5 ± 0,1) x 10^{13} molecules $cm^{-2} yr^{-1}$ from October, 1985 until July, 1990., assuming that the increase is linear. In conjunction with previously published in-situ measurements, we estimate an exponential increase rate of (6.5 ± 0.3) % yr^{-1} from October, 1985 until December, 1992, Using McMurdo Sound measurements, we calculate a south-north interhemispheric ratio of (0,85 ± 0.08).

The method of ratioing the $CHClF_2$ and N_2O columns has been shown to be useful for comparing columns of tropospheric gases at different locations, As shown by comparing Antarctic to TMF column ratios, the effect of different tropopause heights is well compensated for. The good agreement between the column ratios and the in-situ ratios of $CHClF_2$ to N_2O indicates that the systematic error in the spectral linestrengths is probably less than the estimated 10%.

The results of the model simulations illustrate that the difference between the modeled and observed column densities of $CHClF_2$ can be attributed to either uncertainty in the emissions or uncertainties in the OH concentration. For the determination of the OH field using $CHClF_2$ observations to be accurate, the uncertainty in $CHClF_2$ emissions must be reduced. The chemical lifetime of $CHClF_2$ determined by this model is 19.0 years and is consistent with an OH field which is in good

agreement with methyl chloroform observations. This result suggests that historical emissions of $CHClF_2$ are overestimated.

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Table 1: Error sources for a single spectrum

	$CHClF_2$		N_2O
	ATMOS Tbl Mtn	MarkIV McMurdo	ATMOS Tbl Mtn
Random Error Source (%)			
Temperature/Pressure profile	**3**	**3**	2
Signal-to-noise	1	1	1
Assumed VMR profile	**4**	**5**	2
Zero transmission offset	1	1	1
Interfering absorption	6	**2**	2
Total random error	**8**	**6**	4
Systematic Error Source (%)			
Line strengths	10	10	5
Algorithm for column density calculation	3.5	3.5	3,5
Total systematic error	13.5	13.5	8.5

Table 2 Model Calculated $CHClF_2$ Average Concentrations at the end of 1992

Experiment	Change in global OH field(b)	Change in $CHClF_2$ emissions (b)	Global (pptv)	Southern Hemi-sphere (pptv)	Northern Hemi-sphere (pptv)	Global Tropo-sphere (pptv)	Global Strato-sphere (pptv)	Rate of increase (a) $(pptv\ yr^{-1})$
E1	--	--	115	105	123	120	98	6.6
E2	--	-lo%(b)	104	98	111	108	88	5.9
E3	+20%	--	107	100	115	111	90	6.0
E4	+20%	-5%(b)	102	95	109	106	86	5.7
E5	+40%	--	101	94	108	105	85	5.6

(a) Average global rate of increase is calculated from 1982 to 1992. (b) As compared to experiment El. Reduction in $CHClF_2$ emissions is after 1970.

Figure captions

Fig. 1: Assumed $CHClF_2$ and N_2O mixing ratio profiles.

Fig. 2: Typical ATMOS observed and calculated $CHClF_2$ spectra.

Fig. 3: $CHClF_2$ column retrievals (scaled to sea-level) and results of model simulations. See Table 1 for random and systematic errors for Table Mountain and McMurdo measurements, The datum point for MarkIV-McMurdo Sound is the average of 42 measurements taken in September and October, 1986; the error bar represents the 9% standard deviation of the average, For clarity, only modelling experiments E1 (north) and E5 (north) are superimposed on the northern hemisphere results, These two experiments represent the range of results, however, experiments 132 and E4 gave results similar to E5. For the southern hemisphere, only experiment E5 is shown, although E2 and E4 gave similar results.

Fig. 4: $CHClF_2/N_2O$ column and in-situ ratios, Column measurements (this work): ᴏ ATM OS: Table Mountain, CA ▲ Mark IV, McMurdo Sound, Antarctica. Ground-level in-situ measurements (Montzka et al, [1993]): x Niwot Ridge, CO. SAGA cruises: ● N. hemisphere ▣ S. hemisphere. Weighted averages: + N, hemisphere ✱ S. hemisphere, Line fitted for northern hemisphere measurements only,
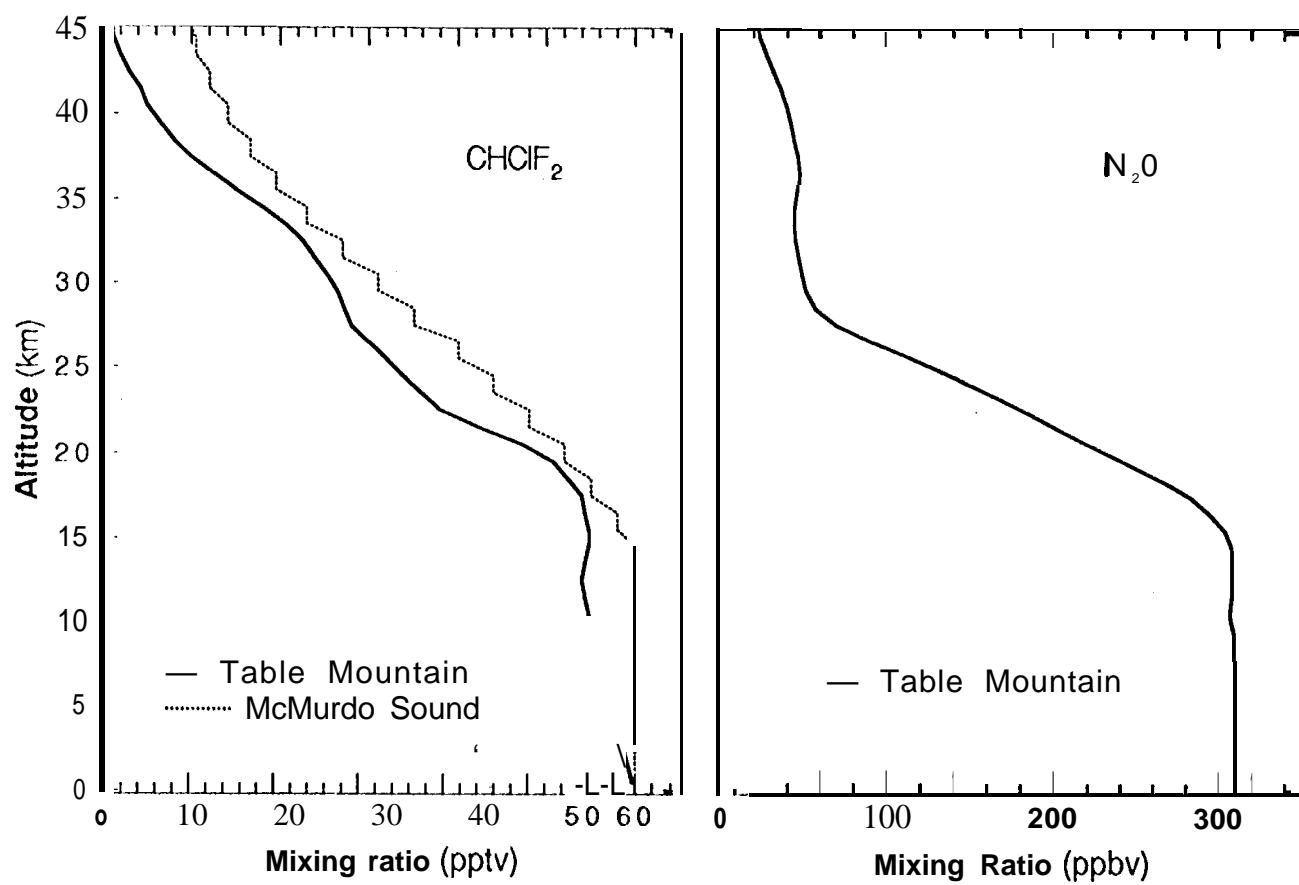
Figure 1

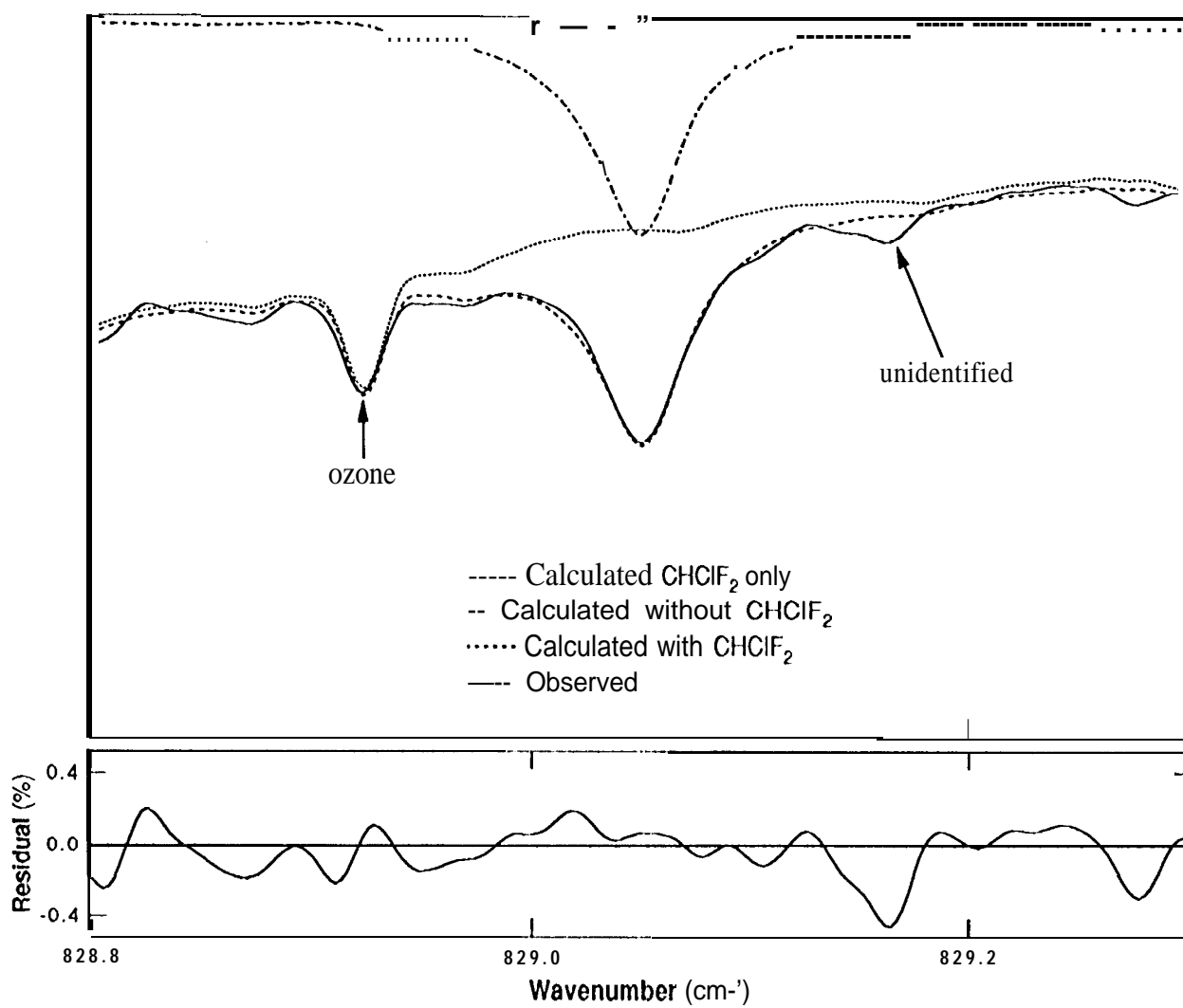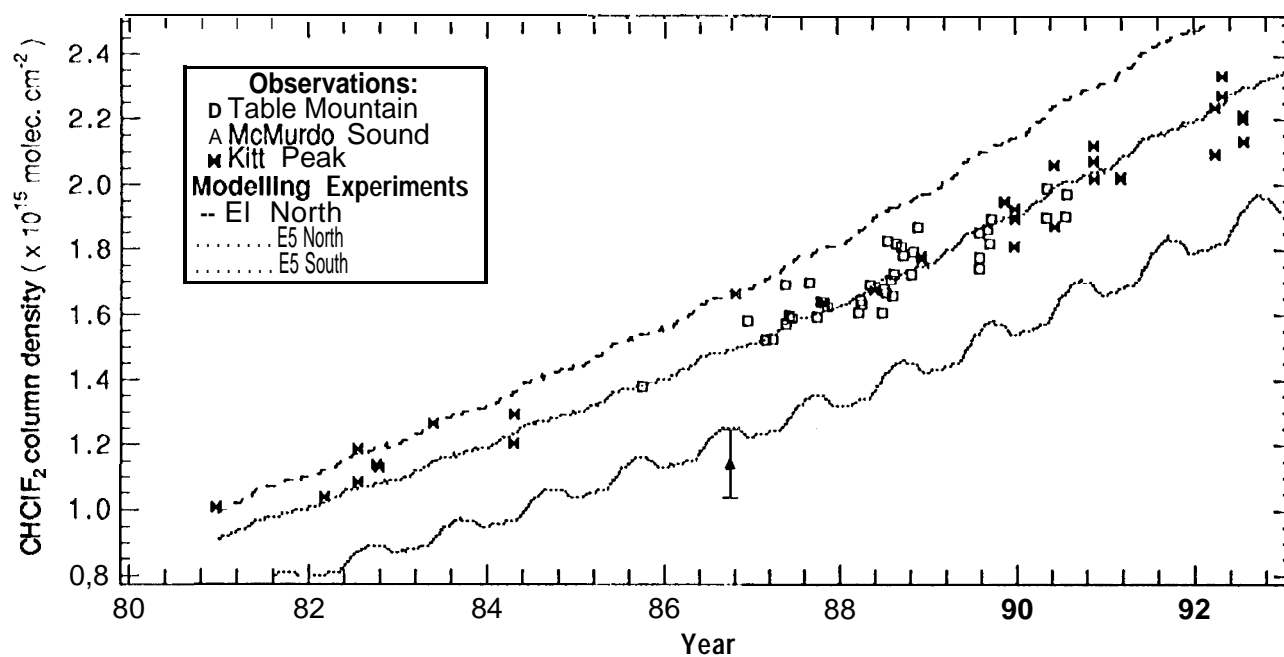----- Calculated CHClF$_2$ only
-- Calculated without CHClF$_2$
····· Calculated with CHClF$_2$
—-- Observed

Figure 2

Figure 3

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Figure 4

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